Short Communication

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Effect of torrefaction pretreatment on the pyrolysis of rubber wood sawdust analyzed by Py-GC/MS

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Abstract

The aim of this study was to investigate the effect of torrefaction on the pyrolysis of rubber wood sawdust (RWS) using pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS). Three typical torrefaction temperatures (200, 250, and 300 °C) and pyrolysis temperatures (450, 500, and 550 °C) were considered. The results suggested that only diethyl phthalate, belonging to esters, was detected at the torrefaction temperatures of 200 and 250 °C, revealing hemicellulose degradation. With the torrefaction temperature of 300 °C, esters, aldehydes, and phenols were detected, suggesting the predominant decomposition of hemicellulose and lignin. The double-shot pyrolysis indicated that the contents of oxy-compounds such as acids and aldehydes in pyrolysis bio-oil decreased with rising torrefaction temperature, implying that increasing torrefaction severity abated oxygen content in the bio-oil. With the torrefaction temperature of 300 °C, relatively more cellulose was retained in the biomass because the carbohydrate content in the pyrolysis bio-oil increased significantly.

Keywords: Torrefaction; Pyrolysis; Bio-oil; Py-GC/MS; Double-shot analysis.

1. Introduction

In recent years, renewable energy has become of growing interest. Biomass is considered as an important renewable fuel and can be processed into other forms of fuel through thermochemical conversion processes such as torrefaction, pyrolysis, gasification, and liquefaction (Chen et al., 2011; Kumar et al., 2017). Pyrolysis converts biomass via thermal degradation in an oxygen-free condition at temperatures between 400 and 650 °C. This results in the production of bio-oils, various gaseous components, and non-volatiles which are further collected as biochars (Bridgwater, 2012). The pyrolytic products include a variety of chemicals such as alkanes, aromatic, hydrocarbons, phenol derivatives, and a few ketones, esters, ethers, sugars, amines, alcohols, etc. It is essential to understand the mechanisms of product formation during the rapid pyrolysis of biomass inasmuch as this can provide the basic information for the selective pyrolysis process to obtain high-grade bio-oils (Chen & Lin, 2016).

One of the potential ways to decrease the oxygen content and improve the quality of bio-oil is to pretreat biomass at a temperature range of 200-300 °C, under atmospheric pressure, and in an inert atmosphere termed torrefaction (Chen et al., 2016; Kumar et al., 2017). Zheng et al. (2014) found that increasing torrefaction temperature of pine wood from 220 to 280 °C decreased the bio-oil yield, but the oxy-compound contents such as acids and aldehydes decreased sharply, while the aromatic hydrocarbon contents increased significantly, leading to an increase in the heating value of bio-oil. Wigley et al. (2016) pretreated wood chips via torrefaction, and found that the char yield was higher following torrefaction and the bio-oil from torrefied biomass was slightly enriched in levoglucosan and aromatics compared to raw bio-oil.

A novel technique to investigate the evolution of the components in biomass in the course of pyrolysis is the pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS).

Py-GC/MS is an important technique for biomass characterization because it can detect pyrolytic products effectively through the comparison of the total chromatographic peak areas obtained at different conditions during the pyrolysis process (Gao et al., 2013). Regarding the applications of Py-GC/MS, Gu et al. (2013) analyzed pyrolysis mechanisms of poplar wood at 600 °C. They proposed that the pyrolytic mechanism of cellulose and hemicellulose was from depolymerization to anhydrosugars and furans or pyranose ring-breaking to light oxygenated species, while the thermal degradation of lignin formed aromatic hydrocarbons. Zhang et al. (2016) discussed the effect of torrefaction pretreatment at two different temperatures (250 and 280 °C) on the pyrolysis products from rice husk. They underlined that the pretreatment decreased the contents of acids, ketones, aldehydes and furans, but significantly increased the contents of sugars, especially levoglucosan. Yang et al. (2014) addressed the effect of torrefaction on switch grass pyrolysis products. Compared to the pyrolysis products of raw switch grass, the contents of anhydrous sugars and phenols in the pyrolysis products of torrefied switch grass were higher. When the torrefaction temperature increased from 230 to 270 °C, the contents of anhydrous sugars and phenols in pyrolysis products increased, whereas the contents of guaiacols decreased.

In recent years, many researches have been carried out on torrefaction pretreatment to improve biomass properties (Chen et al., 2015b), and a few studies have been conducted on the biomass torrefaction followed by pyrolysis, namely, the two-stage thermochemical conversion process. The examination of the literature suggests that Py-GC/MS is a potential tool to investigate the thermal degradation mechanisms of biomass. Though the pyrolysis phenomena of torrefied biomass have been reported in some studies, it should be illustrated that, to date, no research has been carried out on the integration of biomass torrefaction and pyrolysis analyzed by Py-GC/MS. For this reason, the present study aimed to examine the effects of different torrefaction pretreatment temperatures on biomass pyrolysis characteristics. To achieve this target, the thermal degradation behaviors of rubber wood sawdust (RWS) at

different combinations of torrefaction temperatures and pyrolysis temperatures were investigated where a two-stage process using a double-shot pyrolyzer was practiced. In this way, there was no need to interrupt the process when the first stage was completed, and the experiment could directly proceed to the second stage. The detailed information of product formations and reaction mechanisms from the biomass torrefaction followed by pyrolysis was clearly figured out.

2. Experimental

2.1. Raw material and analysis

The raw material used in this study was rubber wood sawdust (RWS), which was obtained from CPC Corporation in Taiwan. The biomass was meshed to sizes less than 1.7 mm, followed by drying in an oven at 105 °C for 24 h to remove moisture. Thereafter, it was stored in sealed plastic bags and placed in a desiccator until experiments were carried out. In the fiber analysis, hemicellulose, cellulose, and lignin contents in the raw RWS were measured, following the method adopted previously (Chen et al., 2010). The analysis indicated that hemicellulose, cellulose, and lignin contents in the RWS were 26.28, 49.14, 13.44 wt%, respectively.

2.2. Py-GC/MS system

The entire system of Py-GC/MS was made up of a pyrolyzer (EGA/PY3030D) and a gas chromatography/mass (GC/MS) spectrometer (Agilent Technologies 7890A/5975C). A two-stage thermal degradation of the RWS by use of a double-shot pyrolyzer was practiced. The pyrolyzer was coupled with the GC/MS to separate and identify the volatiles liberated from the RWS. An ultra-alloy capillary column (30 m–0.25 mm–0.25 μm) was applied in the GC/MS system. The oven temperature was set as follows: (1) 45 °C for 4 min; (2) from 45 to 240 °C at a heating rate of 6 °C min^{-1}; and (3) the capillary column was maintained at 240 °C for about 5 min. High-purity helium at a flow rate of 1.0 mL min^{-1} was used as the carrier gas

and sent into the reaction system. The injector and interface temperatures in the GC/MS were held at 275 and 300 °C, respectively, to identify the pyrolysis volatiles. The mass range used for the mass selective detector was 40–550 m/z. The detected products were identified through a comparison between the experimental mass spectrum and the mass spectrum library attached to the Py–GC/MS apparatus (Wang et al., 2016). To ascertain the measurement quality of the Py-GC/MS system, it was periodically calibrated. Moreover, prior to the experiments certain samples were tested at least twice. The results showed high reproducibility and consistency, revealing the reliability of the measurements.

2.3. Py-GC/MS experimental procedure

In the experiments, three different torrefaction temperatures of 200, 250, and 300 °C, corresponding to light, mild, and severe torrefaction, respectively, were taken into account. Meanwhile, three typical pyrolysis temperatures of 450, 500, and 550 °C (Chen & Lin, 2016) were considered. In each experimental run, about 0.2 mg of the RWS was loaded in a crucible. Then, the crucible was held by a hook to fix its position in the pyrolysis tube. Before the pyrolyzer reached the desired torrefaction temperature, the biomass loaded in the crucial was suspended beyond the pyrolyzer. Once the torrefaction temperature was reached, the crucible was sent into the pyrolyzer for 10 min for the first stage reaction, and produced volatiles were separated and identified by the GC/MS. Afterward, the crucial backed to the location beyond the pyrolyzer. When the pyrolyzer reached the desired pyrolysis temperature, the crucible was sent into the pyrolyzer again for the second stage reaction for 2 min. The produced volatiles were analyzed by the GC/MS (Lee et al., 2005), accomplishing the two-stage reaction.

3. Results and discussion

3.1. Single-shot pyrolysis

In the pyrogram of the RWS pyrolyzed at 500 °C where the abundance of each product was obtained via the Py-GC/MS detected peak area divided by the sample mass, more than 50

peaks were found (E-Supplementary data for this work can be found in e-version of this paper online), and the main compounds, including acids, phenols, ketones, aldehydes, alcohols, carbohydrates, and esters, were listed in **Table 1**. The prime pyrolytic products of the RWS were classified into five groups: acids, phenols, ketones, aldehydes, and carbohydrates. Their weight percentages were 5.38, 14.99, 2.71, 5.64, and 19.25 wt%, respectively. Meanwhile, the principal components contained in pyrolysis volatiles from the RWS have diethyl phthalate, 2,6-dimethoxy-4-allylphenol, coniferyl aldehyde, etc (E-Supplementary data for this work can be found in e-version of this paper online). The acids such as acetic acid (peak #5) (Wenzel, 1970) and the ketones such as 2-cyclopenten-1-one, 2-hydroxy- (peak #6) (Zhao et al., 2016) were assigned to hemicellulose degradation. The phenols such as 2,6-dimethoxy-4-allylphenol (peak #2), 2-methoxy-4-methylphenol (peak #7), 2-methoxy-4-vinylphenol (peak #9), syringol (peak #10), and isoeugenol (peak #12) (Liu et al., 2016) and the aldehydes such as 2,5-dimethoxy-4-methylbenzaldehyde (peak #15) (Arias et al., 2006) were due to lignin degradation. The carbohydrates such as D-Allose (peak #13) and 1,6-anhydro-beta-d-glucopyranose (peak #14) stemmed from cellulose degradation (2017). In the fiber analysis, cellulose accounted for 49.14 wt%. This might be the reason why the weight percent of the carbohydrates was the highest among all the species of volatiles.

3.2. *Double-shot pyrolysis*

3.2.1. First stage torrefaction of double-shot pyrolysis

The TICs of the RWS torrefied at three different temperatures (i.e., 200, 250, and 300 °C) in the first stage suggested that only one peak (#1), namely, diethyl phthalate which pertained to esters, appeared in the pyrograms at the torrefaction temperatures of 200 and 250 °C (E-Supplementary data for this work can be found in e-version of this paper online). The content of diethyl phthalate almost accounted for 100 wt% in the gaseous product from the RWS torrefaction. No other peak signals were observed in the torrefaction pyrograms. This was probably because the biomass was less active at lower torrefaction temperatures, whereby

fewer organic compounds were converted into volatiles (Font Palma, 2013). As described earlier, esters were produced from the thermal degradation of hemicellulose. Accordingly, it was recognized that the single peaks were due to the thermal decomposition of hemicellulose in the RWS (E-Supplementary data for this work can be found in e-version of this paper online). This result was consistent with other studies (Chen & Kuo, 2010; Chen & Kuo, 2011) in which it was underlined that torrefaction had the most profound impact upon hemicellulose when compared with cellulose and lignin. Wenzel (Wenzel, 1970) also highlighted that esters were released from hemicellulose decomposition at 150-300 °C. With the torrefaction temperature of 300 °C, on the other hand, more volatile products in the pyrograms were observed (E-Supplementary data for this work can be found in e-version of this paper online), and their relative peak areas were listed in **Table 2**. It could be seen that aldehydes such as coniferyl aldehyde (peak #3) and 3,5-dimethoxy-4-hydroxycinnamaldehyde (peak #4), phenols such as 2,6-dimethoxy-4-allylphenol (peak #2), isoeugenol (peak #12), and esters such as diethyl phthalate (peak #1) were the most prominent products in that their weight percentages in the torrefaction product were 19.53, 9.58, and 35.15 wt%, respectively. In **Table 2**, coniferyl aldehyde was responsible to 42.85% of the aldehyde volatiles. This agreed with the observation of Arias et al. (2006) where it was reported that the major signal in pyrograms at temperatures of 250 and 300 °C was coniferyl aldehyde, resulting from the thermal decomposition of lignin. Rousset et al. (2009) also studied lignin structure at 280°C using thioacidolysis method and showed intense structural transformations with the following degradation reactions: (1) the cleavage of lignin β-O-4 bonds; (2) a severe recondensation reactions, which led to considerable enrichment of resistant interunit bonds in the thermally-treated lignin; (3) the formation of vinyl ether structures through the loss of the terminal hydroxymethyl groups from lignin sidechains; the liberated formaldehyde then participated in crosslinking the polymer according to similar mechanisms to those of heat-hardened formo-phenolic resins; and (4) to a lesser extent, the oxidative cleavage of the

Cα-Cβ benzylic bonds with the formation of benzoic acid and benzoic aldehyde end-groups in lignin. By virtue of notable production of esters, aldehydes, and phenols, it followed that the formation of volatiles was owing to predominant decomposition of hemicellulose and lignin at this temperature (i.e., 300 °C). In contrast, carbohydrates such as 1,6-anhydro-beta-d-glucopyranose (peak #14) merely accounted for 3.07 wt%. This implied, in turn, that the thermal decomposition of cellulose in the RWS was not pronounced. Overall, the pyrograms at 200, 250, and 300 °C (E-Supplementary data for this work can be found in e-version of this paper online), qualitatively agreed with the observations of Chen et al. (2011) where they observed that the GC/MS spectra of the condensed liquids from Lauan torrefied at 200 and 250 °C were similar to each other, whereas there was a notable difference in the spectrum at 300 °C from the preceding two temperatures.

3.2.2. Second stage pyrolysis of double-shot pyrolysis

A comparison to the pyrogram of single stage reaction indicated that less peaks were detected in multiple stage reaction (E-Supplementary data for this work can be found in e-version of this paper online), especially for those at longer retention time (> 30 min) where the peaks of aldehydes (e.g., peaks #3, 4, 15, 16), stemming from lignin degradation (Arias et al., 2006), in the pyrograms were abated. This was presumably attributed to some components in the biomass being preliminarily decomposed from torrefaction so as to produce less compounds from the second stage pyrolysis. The comparison between the three figures of the multiple stage reaction (E-Supplementary data for this work can be found in e-version of this paper online), suggested that the number of peaks had a trend to diminish when the retention time was larger than 25 min, especially for the pyrolysis of the biomass torrefied at 300 °C. An increase in torrefaction temperature intensified lignin decomposition. This was the reason why the peaks of phenols (e.g., peaks #7, 8, 9, 10, 12) at the retention time of 23-30 min decreased at higher torrefaction temperatures. This reflected that torrefaction was able to make the properties of the biomass more uniform so that relatively less compounds were

generated from its pyrolysis. In summary, the pyrolytic product distributions from the RWS changed to a certain extent when torrefaction was applied, especially under severe torrefaction. This behavior was also observed by Wang et al. (2017) who examined the pyrolysis behavior of cellulose through GC/MS analysis.

The relative contents of different groups of chemicals (i.e., acids, phenols, ketones, aldehydes, and carbohydrates) from the pyrolysis of the torrefied RWS are profiled in **Fig. 1a** where the chemicals produced from the single stage pyrolysis are also shown for comparison. Acids were a major constituent of the volatiles produced from hemicellulose pyrolysis. An increase in torrefaction temperature intensified the thermal degradation of hemicellulose. This the reason why a decent in acid content was exhibited when the torrefaction temperature went up where the acetic acid was the prime constituent in the acids (**Table 1**). Phenols and aldehydes were the main pyrolytic products from the thermal degradation of lignin. Torrefaction also had an impact upon lignin decomposition (Chen et al., 2015). Phenols and aldehydes had a trend to decrease with rising torrefaction temperature, revealing that lignin in the RWS was also sensitive to the torrefaction temperature. It was known that oxy-compounds such as acids and aldehydes might cause bio-oil instability. Their yields decreased with increasing torrefaction temperature, implying that increasing torrefaction severity could abate the oxygen content and improve bio-oil quality (Wigley et al., 2016). The decrease in phenols under higher torrefaction temperatures was in line with the result of Gogoi et al. (2017) where they pointed out that an increase in torrefaction temperature and time might decrease the yield of phenols, resulting from lignin decomposition and carbonization during the torrefaction process. As for the cellulose in the RWS, the influence of torrefaction at 250 °C upon cellulose was more than that at 200 °C. As a consequence, relatively more cellulose was retained in the torrefied biomass at 200 °C and the carbohydrate content in the pyrolytic product was higher. With regard to the RWS undergoing torrefaction at 300 °C, the

carbohydrate content was by far higher than the other biomass samples, presumably due to higher thermal resistance of cellulose at 300 °C when compared to hemicellulose and lignin.

3.3. Different combinations of torrefaction and pyrolysis temperatures

To proceed farther into the recognition of the formation characteristics of pyrolytic products from torrefied biomass, three different combinations of torrefaction and pyrolysis temperatures, namely, (torrefaction, pyrolysis) = (200 °C, 450 °C), (250 °C, 500 °C), and (300 °C, 550 °C), were taken into consideration, and their pyrograms (E-Supplementary data for this work can be found in e-version of this paper online), were compared with each other. Upon inspection of the pyrograms, the number of peaks decreased with increasing combined temperatures when the retention time was longer than 25 min. This behavior was similar to the pyrograms observed earlier. It followed that the torrefaction temperature played a pronounced role on the pyrolysis of the RWS, regardless of the pyrolysis temperature. An examination on the relative contents of the five different groups of compounds shown in **Fig. 1b** suggested that phenols and carbohydrates accounted for the larger shares in the pyrolytic products. This revealed that relatively more lignin and cellulose were retained in the torrefied biomass, especially for cellulose in the biomass torrefied at 300 °C. A comparison between **Fig. 1a** and **Fig. 1b** at the torrefaction temperature of 200 °C indicated that produced carbohydrates at the pyrolysis temperature of 450 °C had a lower yield (15.29 wt%, **Fig. 1b**) than the pyrolysis temperature of 500 °C (18.37 wt%, **Fig. 1a**). This could be explained by less cracking of cellulose in the course of pyrolysis. Alternatively, with the torrefaction temperature of 300 °C, the produced carbohydrates at the pyrolysis temperature of 500 °C had a higher yield (26.81 wt%, **Fig. 1a**) than the pyrolysis temperature of 550 °C (23.7 wt%, **Fig. 1b**), presumably due to more products formed from lignin degradation in the latter. The entire profiles of phenols and carbohydrates in **Fig. 1b** were similar to those in **Fig. 1a**. This implied, in turn, that torrefaction played a pivotal role in producing chemicals from biomass pyrolysis.

4. Conclusions

The Py–GC/MS analysis suggested that hemicellulose in the RWS was obviously degraded from the torrefaction at 200 and 250 °C, and lignin decomposition was also pronounced at 300 °C. The double-shot technique further indicated that the contents of acids and aldehydes in pyrolysis vapor decreased with rising torrefaction temperature, and the pyrograms depicted that less compounds were contained in the pyrolysis bio-oils. This revealed that torrefaction could make bio-oil more uniform and reduce its oxygen content. Carbohydrates in pyrolysis vapor increased significantly from the biomass torrefied at 300 °C, implying that more cellulose was retained in the torrefied biomass.

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340 **Table 1.** Relative peak area distribution of the main products for biomass in Py-GC/MS

Bio-oil fraction	Formula		Relative content (%)					
			Single stage	Two stage				
			500 °C	200 °C		250 °C	300 °C	
				450 °C	500 °C	500 °C	500 °C	550 °C
Acid	Acetic acid	$C_2H_4O_2$	5.38	10.71	8.10	7.11	6.11	7.59
Phenols	Phenol, 2-methyl-	C_7H_8O	0.11	1.08	-	0.44	-	-
	Phenol, 4-methyl-	C_7H_8O	0.24	-	-	0.42	-	-
	Phenol, 2-methoxy-	$C_7H_8O_2$	0.81	-	2.65	2.94	1.92	-
	2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	0.90	1.78	2.14	2.41	2.49	1.25
	3-Methoxycatechol	$C_7H_8O_3$	1.43	2.08	-	1.20	1.71	1.50
	4-Ethyl-2-methoxyphenol	$C_9H_{12}O_2$	0.42	0.49	-	0.60	0.52	-
	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	1.34	1.85	2.40	1.77	1.52	0.90
	Syringol	$C_8H_{10}O_3$	1.68	2.37	1.30	3.68	3.18	3.47
	4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	$C_{10}H_{12}O_3$	1.94	0.44	6.08	-	-	-
Ketones	2-Cyclopenten-1-one, 2-hydroxy-	$C_5H_6O_2$	1.25	1.71	1.85	2.20	1.83	2.38
	1,2-Cyclopentanedione, 3-methyl-	$C_6H_8O_2$	-	-	-	1.12	0.76	-
Aldehydes	Butanedial	$C_4H_6O_2$	-	-	1.34	-	1.12	1.61
	Furfural	$C_5H_4O_2$	0.72	0.99	-	0.99	0.94	-
	Vanillin	$C_8H_8O_3$	0.73	0.35	0.71	0.36	-	-
	2,5-Dimethoxy-4-methylbenzaldehyde	$C_{10}H_{12}O_3$	1.59	-	1.84	2.96	-	2.76
	3,5-Dimethoxy-4-hydroxybenzaldehyde	$C_9H_{10}O_4$	1.10	0.78	2.89	0.56	0.36	-
	3,5-Dimethoxy-4-hydroxycinnamaldehyde	$C_{11}H_{12}O_4$	0.92	1.09	0.85	0.19	-	-
Carbohydrates	1,4:3,6-Dianhydro-α-d-glucopyranose	$C_6H_8O_4$	0.51	0.38	-	0.39	0.47	0.58
	D-Allose	$C_6H_{12}O_6$	14.37	14.91	15.92	3.93	25.09	23.12
	1,6-anhydro-beta-d-glucopyranose	$C_6H_{10}O_5$	4.37	-	2.45	10.45	1.25	-
Benzenes	Benzene,4-methoxy-2-methyl-1-(methylthio)-	$C_9H_{12}OS$	1.22	1.86	-	-	-	2.86
Esters	Diethyl Phthalate	$C_{12}H_{14}O_4$	-	-	7.20	-	5.04	-

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344 **Table 2.** Relative peak areas of main products from biomass torrefaction in Py-GC/MS.

Bio-oil fraction	**Relative content (%)**		
	200 °C	**250 °C**	**300 °C**
Phenols	**-**	**-**	**9.58**
2-Methoxy-4-vinylphenol	-	-	1.41
Syringol	-	-	0.55
Isoeugenol	-	-	1.92
2,6-Dimethoxy-4-allylphenol	-	-	5.70
Aldehydes	**-**	**-**	**19.53**
4-Methyl-2,5-dimethoxybenzaldehyde		-	2.41
3,5-Dimethoxy-4-hydroxybenzaldehyde		-	1.06
coniferyl aldehyde		-	8.37
3,5-Dimethoxy-4-hydroxycinnamaldehyde		-	7.69
Carbohydrates	**-**	**-**	**3.07**
1,6-Anhydro-β-D-glucopyranose(levoglucosan)	-	-	3.07
Esters	**100**	**100**	**35.15**
Diethyl Phthalate	100	100	35.15
Alcohols	**-**	**-**	**2.09**
Homovanillyl alcohol	-	-	0.44
2',4',6'-Trihydroxy-3'-methylbutyrophenone	-	-	1.65

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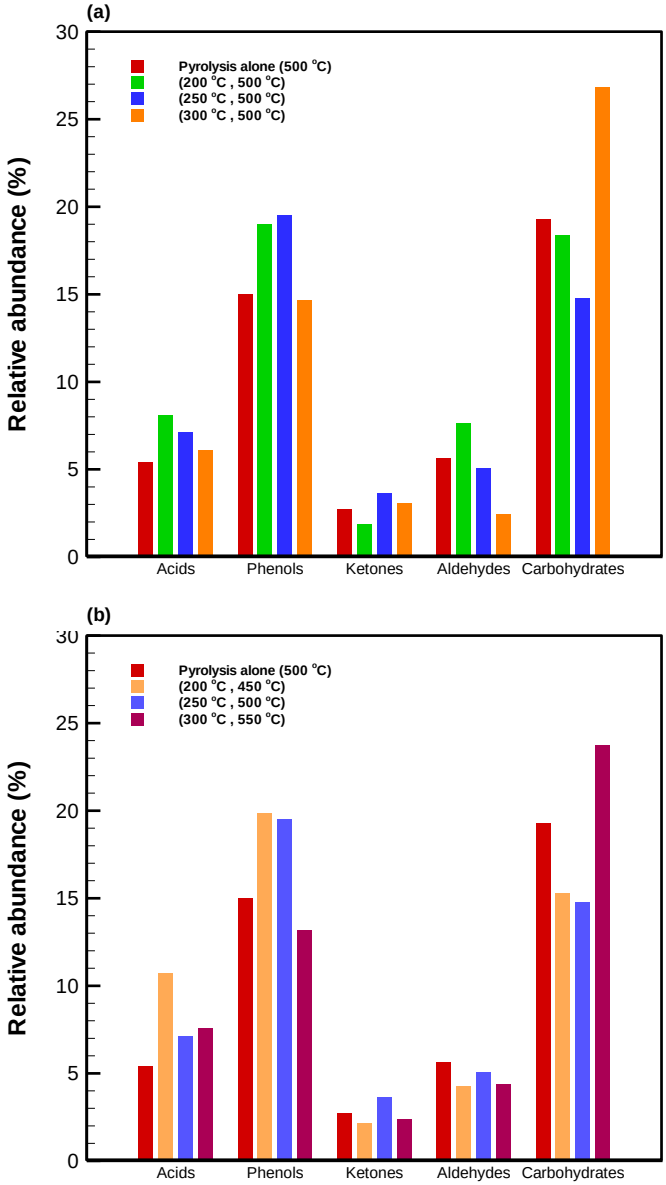
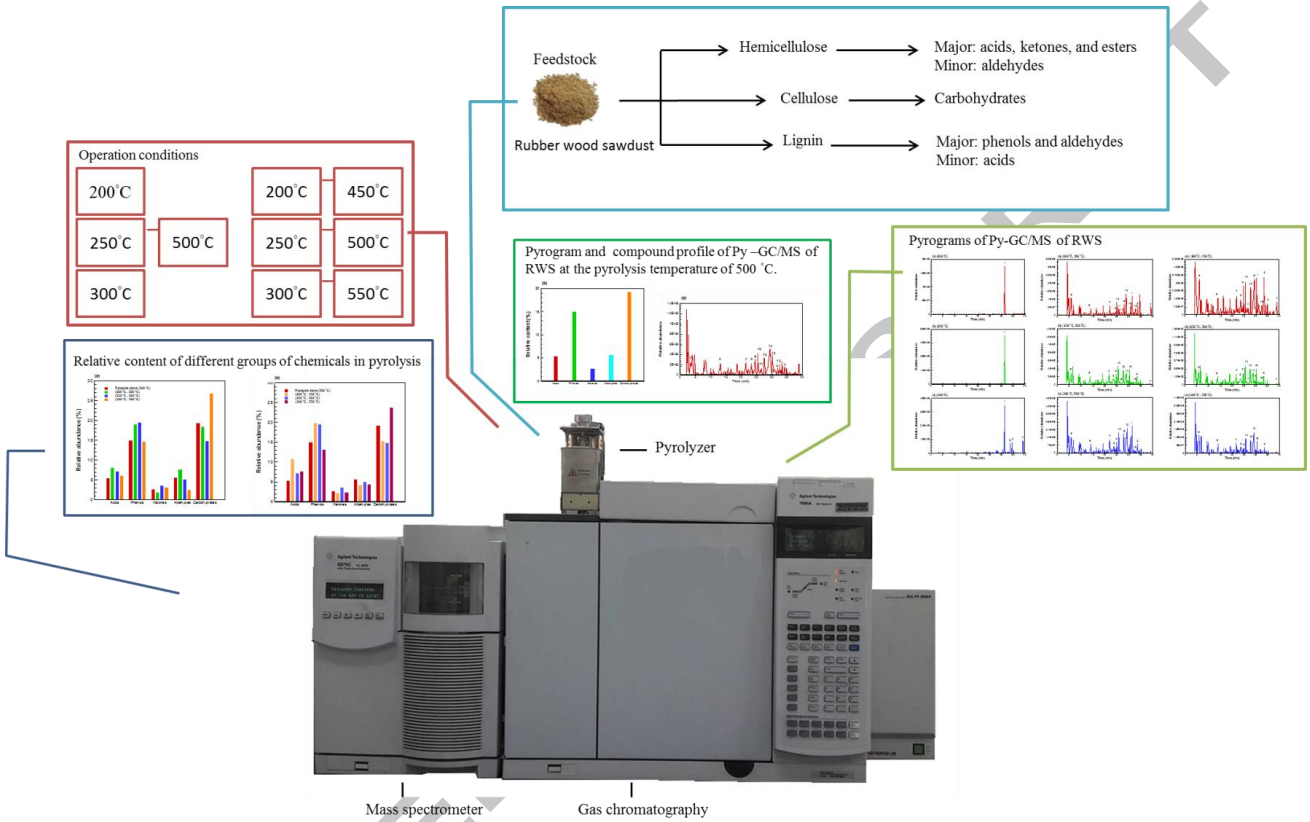


Fig. 1. Relative content profiles of five groups of compounds at the pyrolysis temperature of 500 °C along with the torrefaction temperatures of (a) 200 °C, (b) 250 °C, and (c) 300 °C.

Graphical abstract



Highlights

1. Effect of torrefaction on the pyrolysis of rubber wood sawdust is analyzed using Py-GC/MS.
2. Hemicellulose degradation is exhibited at torrefaction temperatures of 200 and 250 °C.
3. Hemicellulose and lignin decomposition is predominant for the biomass torrefied at 300 °C.
4. Acids and aldehydes contents in pyrolysis bio-oil decrease with torrefaction temperature.
5. Relatively more cellulose is retained in the biomass when it is torrefied at 300 °C.